



Promoting Pd-catalyzed Suzuki coupling reactions through near-infrared plasmon excitation of WO_{3-x} nanowires



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ABSTRACT

We have prepared Pd-loaded plasmonic WO_{3-x} nanowires with retained strong plasmon absorption in the visible and NIR region, and demonstrated that the plasmon excitation of WO_{3-x} nanowires by long wavelength irradiation can greatly promote Suzuki coupling reactions catalyzed by the attached Pd nanoparticles in terms of the main product yield and selectivity, which is attributed to the photothermal effect with strong localized plasmon heating on the WO_{3-x} nanowire surface. Our studies reveal that the contributions of plasmon excitation can not only affect the reactions directly involving the plasmonic structure itself, but also assist the reactions catalyzed by the third-part materials attached on the plasmonic structure surface.

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1. Introduction

In the past decade, the magic of localized surface plasmon resonance (LSPR) has attracted great interest because of its unique effect on promoting various activities including spectroscopic responses (e.g., Raman and fluorescence), photovoltaics, and photocatalysis [1–3]. In particular, researchers have demonstrated that the LSPR excitation of noble metal particles can effectively promote catalytic reactions occurring on their surfaces with better yield and selectivity [4,5]. However, in order to obtain the optimal reaction efficiency, one would encounter the challenge of balancing the particle size of noble metals because high catalytic activity requires very small particle size, while contrarily, strong LSPR absorption normally occur on relatively large particles [6]. One of the solutions is incorporating two segments to separate the plasmonic effect and catalytic surface. For example, Pd-decorated Au nanostructures showed plasmon enhanced efficiency for Suzuki coupling reaction and formic acid dehydrogenation [7]. Hydrogen generation activity over Pt-decorated Au rods can be greatly enhanced by visible-light-driven LSPR excitation [8]. Nevertheless, the decoration of Pd or Pt on plasmonic gold surfaces likely causes dampening of LSPR and interfacial alloy formation, giving negative effect on the use of LSPR for chemical reactions.

Recently, researchers have found that some metal oxide nanostructures, such as WO_{3-x} , MoO_{3-x} , and TiO_{2-x} , can also exhibit LSPR in the visible and near-infrared (NIR) region due to abundant oxygen vacancies or heavy doping, and showed that the NIR LSPR excitation is capable of driving photocatalytic reactions [9–11]. These plasmonic metal oxides provide great opportunities to attain both strong LSPR absorption for plasmon enhancement and high catalytic activity via loading of small metal nanoparticles onto their surfaces. By this way, it would be possible to utilize LSPR excitation of metal oxides to enhance the yield and selectivity of chemical reactions catalyzed by the loaded metal particles. Herein, in this work, we deposit Pd nanoparticles onto plasmonic WO_{3-x} nanowires with well-retained LSPR absorption in the visible and NIR region, and demonstrate that the LSPR excitation of WO_{3-x} nanowires under long wavelength ($\lambda > 650$ nm) irradiation significantly promotes the Suzuki coupling reaction catalyzed by Pd nanoparticles in terms of the main product yield and selectivity. The contribution of LSPR excitation is primarily attributed to the photothermal effect with strong localized plasmon heating on the WO_{3-x} nanowire surface.

2. Experimental

2.1. Preparation of Pd/ WO_{3-x} nanowires

WO_{3-x} nanowires were synthesized according to our previous work [12]. In a typical procedure, 30 mg hexacarbonyltungsten

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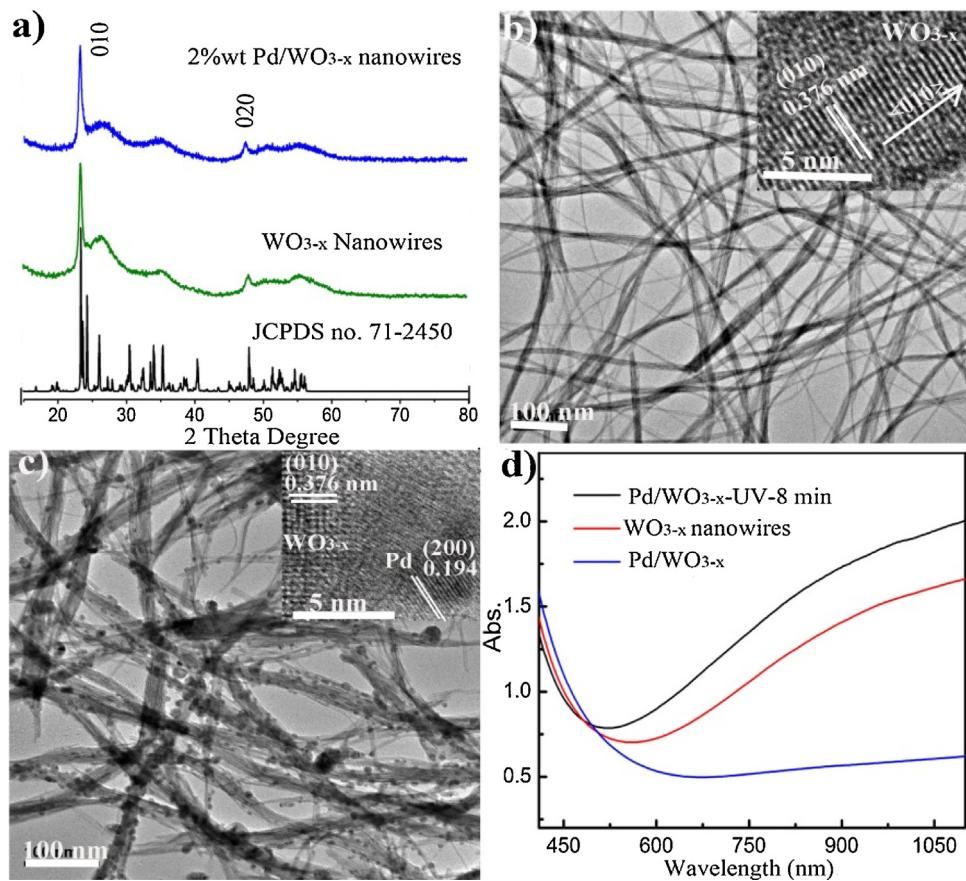


Fig. 1. (a) XRD patterns of as-synthesized WO_{3-x} , 2 wt% Pd/ WO_{3-x} and standard tungsten oxides (JCPDS no. 71-2450); (b) and (c) TEM and HRTEM images of WO_{3-x} nanowires and 2 wt% Pd-loaded WO_{3-x} nanowires; (d) light absorption spectra (400–1100 nm) of WO_{3-x} nanowires (red line), 2 wt% Pd/ WO_{3-x} (blue line) and 2 wt% Pd/ WO_{3-x} after 8-min UV-irradiation (black line) in ethanol. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

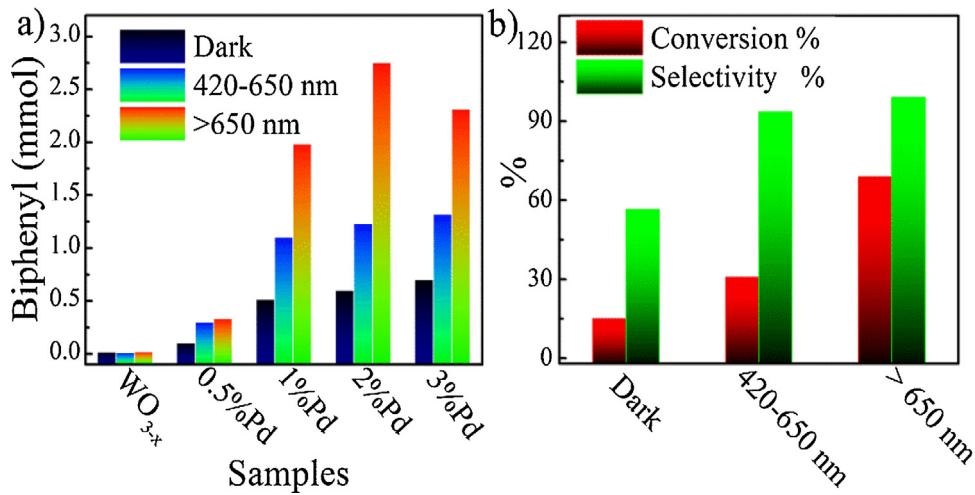


Fig. 2. (a) The biphenyl product yield over different amount of Pd (0, 0.5 wt%, 1 wt%, 2 wt% and 3 wt%) loaded WO_{3-x} nanowires under dark, visible (420–650 nm) and near-IR light (>650 nm) irradiation; (b) conversion of iodobenzene and selectivity of biphenyl for Suzuki coupling reaction (1) over 2 wt% Pd/ WO_{3-x} nanowires under dark and different light (>650 nm and 420–650 nm) irradiation. Reaction time: 100 min.

$\text{W}(\text{CO})_6$ were dissolved into 80 ml absolute ethanol and yellow precursor solution was obtained. Then 40 ml of the above solution was transferred to 80 ml teflon-lined autoclave and followed by solvothermal treatment at 160 °C for 12 h. The product samples were separated from solution by centrifugation, washed with ethanol for two times and dried in a vacuum oven. For loading of Pd nanoparticle, 20 mg WO_{3-x} nanowires were dispersed into

20 ml ethanol under ultrasonication for 10 min. Different volume of $\text{Pd}(\text{NO}_3)_2$ solution (20 mM) was added into the suspension under stirring. Subsequently, 0.4 ml freshly prepared NaBH_4 solution (0.1 M) was injected. After constant stirring for 2 h, the products were collected via centrifugation, washed with ethanol for two times and dried in a vacuum oven.

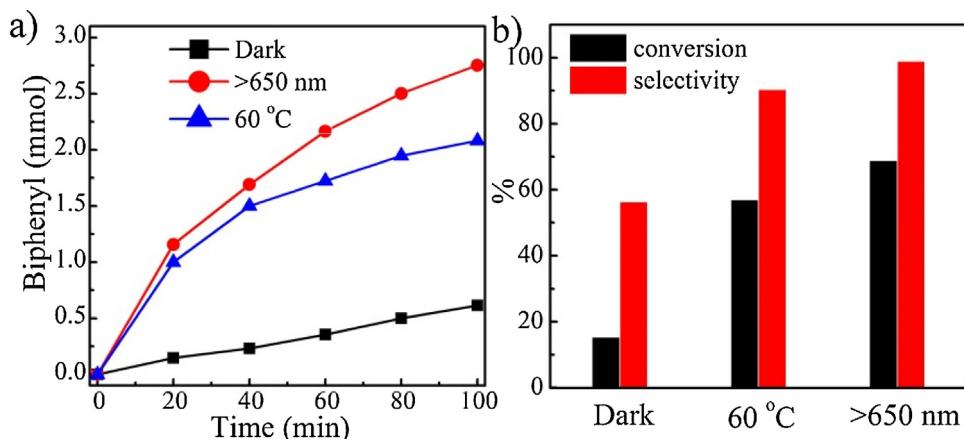


Fig. 3. (a) Yield of biphenyl and (b) conversion of iodobenzene and selectivity of biphenyl for Suzuki coupling reaction (1) over 2 wt% Pd/WO_{3-x} under dark, heating at 60 °C, and irradiation of long wavelength light (>650 nm). Reaction time: 100 min.

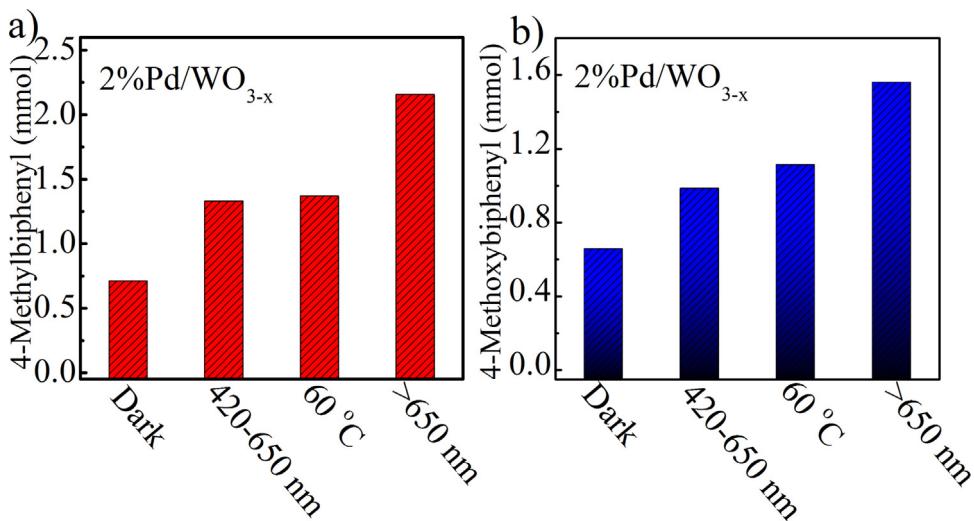


Fig. 4. Yield of 4-methylbiphenyl (a) and 4-methoxybiphenyl (b) over 2 wt% Pd/WO_{3-x} under dark, heating at 60 °C, visible (420–650 nm) and long wavelength (>650 nm) light irradiation. Reaction time: 100 min.

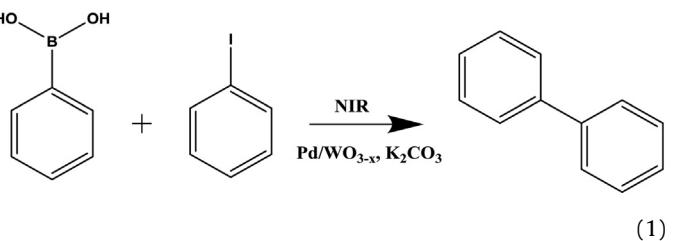
2.2. Characterization

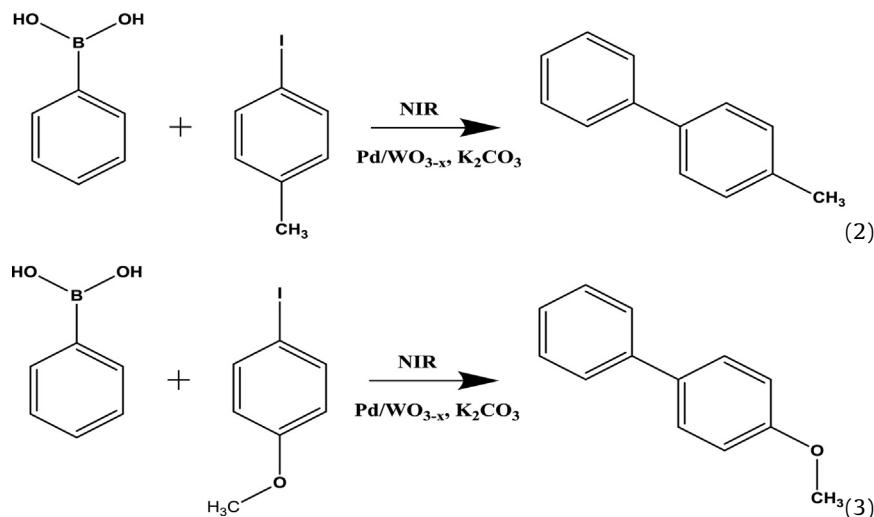
The X-ray diffraction (XRD) patterns of samples were recorded on Bruker D8 ADVANCE powder diffractometer using Cu-K α radiation ($\lambda = 0.1542$ nm) at a scanning rate of 5°/min in the region of $2\theta = 20\text{--}80^\circ$. Transmission electron microscopy (TEM) measurements were carried out by JEM-2010 microscope. The absorption spectra were obtained on a UV-vis UV-2501 Spectrophotometer (Shimadzu). The actual amount of Pd loading was estimated by energy-dispersive X-ray (EDX) spectroscopy.

2.3. Suzuki coupling reactions

Suzuki coupling reaction was conducted in a photocatalytic reaction system. A 50-ml quartz tube was used as reaction cell. The Pd/WO_{3-x} (20 mg) nanowires were dispersed into 20 ml absolute ethanol in reaction cell under ultrasonication for 10 min. Then the cell was sealed with a rubber stopper. After degassing for 20 min by N₂ using needles, the cell was stirred with a magnetic stirrer and irradiated under UV-light supplied by a 300-W xenon lamp for 10 min to recover the LSPR absorption of WO_{3-x} nanowires. For the Reaction (1), the reactants including 0.4 ml iodobenzene, 0.4 g phenylboronic acid and 0.4 g K₂CO₃, were added into the suspension with continuous degassing for 20 min by N₂. The cell was

irradiated under 500 W xenon lamp coupled with different optical filters for the Suzuki coupling reaction. For the Reactions (2) and (3), the iodobenzene was replaced by 4-iodotoluene (0.7 g) and 4-iodoanisole (0.75 g), respectively, and the reactions were carried out under the same conditions. After reaction, 1.5 ml solution was collected and filtered through a Millipore filter (pore size 0.45 μ m) to remove the insoluble species. The products were analyzed by an Agilent HP-7890A gas chromatography (GC) with HP-5 (19,091J-413, 30 m \times 0.320 mm, 0.25 μ m) column. An Agilent 6890N GC equipped with mass spectrometer was used to identify the products.





3. Results and discussion

WO_{3-x} nanowires were synthesized through solvothermal treatment of the ethanol solution of $\text{W}(\text{CO})_6$ at 160°C for 12 h [12]. Pd nanoparticles were loaded on the surface of WO_{3-x} nanowires via reduction of $\text{Pd}(\text{NO}_3)_2$ by NaBH_4 in the ethanol suspension of WO_{3-x} nanowires. (See Supporting information for details) The X-ray diffraction (XRD) pattern (Fig. 1a) of the obtained WO_{3-x} nanowires well matches the standard XRD pattern of monoclinic $\text{W}_{18}\text{O}_{49}$ (JCPDS no. 71-2450). The strong (0 1 0) peak indicates the preferential growth of WO_{3-x} along $\langle 0 1 0 \rangle$ directions. Loading of small amount of Pd nanoparticles did not alter the XRD pattern. The signature peaks of Pd were not observed due to very small size and limited amount of Pd nanoparticles. The transmission electron microscopy (TEM) examinations (Fig. 1b and Fig. S1) prove the nanowire morphology of the obtained WO_{3-x} samples with lengths of several micrometers and diameters of ~ 10 nm. The high-resolution TEM (HRTEM) image (inset of Fig. 1b) shows clear lattice fringe of 0.376 nm, corresponding to the (0 1 0) interplanar spacing of $\text{W}_{18}\text{O}_{49}$ [13]. Fig. 1 and Fig. S1b show that the Pd-loading does not change the nanowire features and the deposited nanoparticles have an average diameter of 5 nm. The HRTEM analysis (inset of Fig. 1c) of the nanoparticles reveals clear lattices fringes of 0.194 nm which matches the (2 0 0) interplanar spacing of metallic Pd.

The obtained WO_{3-x} nanowires appear blue color when suspended in an ethanol solution (Fig. S2). The UV-vis spectrum (Fig. 1d) shows their LSPR absorption starting from 520 nm to NIR region [10,12]. During the nanowire formation, some surface W^{6+} species are reduced to W^{5+} as proven by the XPS analyses in our previous work [12], leading to abundant surface oxygen vacancies with increased free electron density. The collective oscillation of the free electrons on WO_{3-x} nanowire surfaces results in strong absorption in the visible and NIR region, which is similar to the LSPR of noble metal particles [14]. As such, the obtained samples can be considered as plasmonic WO_{3-x} nanowires. Right after loading of Pd nanoparticles, though the suspension still appears blue, the LSPR absorption of WO_{3-x} nanowires becomes weaker because some surface W^{5+} species are oxidized by the Pd^{2+} . However, this plasmon absorption of $\text{Pd}/\text{WO}_{3-x}$ nanowires can be readily recovered by simple UV-irradiation for a few minutes, as shown in Fig. 1d, because the surface oxygen vacancies can be re-generated via UV-driven photocatalytic reduction of surface W^{6+} by ethanol [15].

In literature, the NIR LSPR absorption of metal oxide nanocrystals has been used in photothermal therapy to kill tumor and cancer cells [16,17]. However, due to the low photon energy, the excitation of NIR LSPR has limited ability of contributing to

photocatalytic or catalytic reactions even though the solar spectrum has large portion of NIR region. Previous researchers have attempted to utilize the large Au or Pd nanostructures having NIR plasmon absorption to promote catalytic reactions under NIR irradiation for LSPR excitation. However, the catalytic activities of the large metal nanocrystals are fairly low, which conversely weakens the effect driven by LSPR excitation. In contrast, in this work, the $\text{Pd}/\text{WO}_{3-x}$ nanowires enable advantages of both high catalytic activity from small Pd nanoparticles and NIR plasmon absorption from WO_{3-x} nanowires, allowing for promoting catalytic reactions on Pd through NIR LSPR excitation of WO_{3-x} .

Herein, we choose Suzuki coupling reaction for proof-of-concept, and demonstrate that the NIR plasmon excitation of WO_{3-x} nanowires can enhance the Pd-catalyzed Suzuki coupling reactions which have been well known as efficient synthetic route to obtain biphenyl derivatives [18]. A typical Suzuki coupling Reaction (1) was carried out by using Iodobenzene (0.4 ml) and phenylboronic acid (0.4 g) as reactants, K_2CO_3 (0.4 g) as base, and $\text{Pd}/\text{WO}_{3-x}$ nanowires (20 mg) as the catalyst. We have investigated the yield and selectivity of the target product biphenyl during 100-min reaction in dark and under light irradiation (>650 nm or 420–650 nm), respectively. Note that irradiation below 420 nm causes strong bandgap excitation of WO_{3-x} nanowires, leading to fast degradation of iodobenzene without generating the biphenyl product (Fig. S3).

Fig. 2a shows the yield of biphenyl with respect to the Pd loading amount on WO_{3-x} . The detailed data are listed in Table S1 of Supporting information. The actual loading amount of Pd was estimated by EDX spectroscopy and the results were given in Table S2 of Supporting information. Pure WO_{3-x} nanowires have no activity for Suzuki coupling. The Pd-loaded WO_{3-x} nanowire samples with different Pd loading amount (0.5–3 wt%) are all active to catalyze the Suzuki coupling in dark, and the biphenyl yield increases along with higher Pd loading amount. If visible-light irradiation (420–650 nm) is introduced during the reaction, the biphenyl yields for all $\text{Pd}/\text{WO}_{3-x}$ samples are almost double as compared to the yields in dark. Significantly, when the reaction is carried out under longer wavelength (>650 nm) irradiation, the biphenyl yields are further greatly promoted for all $\text{Pd}/\text{WO}_{3-x}$ samples even though the photon energy is lower. Among all samples, the 2 wt% Pd/ WO_{3-x} nanowires exhibit the optimal biphenyl yield under long wavelength (>650 nm) irradiation, and thereby selected as the key sample for further mechanistic studies. Moreover, in addition to the biphenyl yield, the long wavelength (>650 nm) irradiation leads to apparently higher conversion of iodobenzene

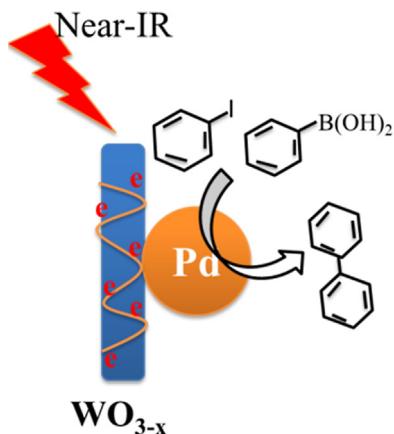


Fig. 5. Schematic illustration of plasmon enhanced Suzuki coupling reaction over Pd/WO_{3-x} nanowires.

and selectivity of biphenyl than dark condition and visible-light (420–650 nm) irradiation, as shown in Fig. 2b. These results indicate that the strong plasmon excitation (>650 nm) of WO_{3-x} nanowires can promote the Pd-catalyzed Suzuki coupling reaction between phenylboronic acid and iodobenzene with better biphenyl yield and higher selectivity. In comparison, the control sample, 2 wt% Pd-loaded WO_{3-x} without plasmonic absorption (passivated by O₂ treatment), showed much lower biphenyl yield even under light irradiation (Fig. S4).

Here, it is believed that the contribution of plasmon excitation is dominated by the photothermal effect. It means that the photon energy by plasmonic absorption is mainly converted to thermal energy, leading to increase of environmental temperature. It is known that Suzuki coupling is a thermal-driven catalytic process and strongly affected by reaction temperature. Under long-wavelength (>650 nm) irradiation, the temperature of the solution containing 2 wt% Pd/WO_{3-x} nanowires increases from 25 °C to 60 °C in 10 min due to strong plasmon absorption and is kept at ~60 °C thereafter. In contrast, without any catalyst, the solution temperature only slightly increases under the same irradiation. As such, we used the 2 wt% Pd/WO_{3-x} nanowires to carry out a control reaction of Suzuki coupling at 60 °C in dark. We found that the conversion of iodobenzene, yield and selectivity of biphenyl product are all higher than that at room temperature, but interestingly, still clearly lower than that under long wavelength (>650 nm) irradiation (Fig. 3).

The plasmonic effect of 2 wt% Pd/WO_{3-x} nanowires can be further extended to the other Suzuki cross coupling reactions involving derivatives of iodobenzene (4-iodotoluene or 4-iodoanisole) as described by Reactions (2) and (3). As shown in Fig. 4, the yield and selectivity of both reaction products (4-methylbiphenyl and 4-methoxybiphenyl) under irradiation of long wavelength light (>650 nm) are higher than that under other conditions including dark, heating (60 °C), and visible light (420–650 nm) irradiation. The detailed data are listed in Fig. 3 of Supporting information. These results further confirm that the plasmon excitation of WO_{3-x} nanowires can enhance the Pd-catalyzed Suzuki coupling reaction in terms of reaction yield and main product selectivity. Further, more importantly, for both Reactions (2) and (3), the long wavelength (>650 nm) irradiation led to much higher yield of the main product as compared to the 60 °C reaction condition. These results suggest that the promoted Suzuki coupling by plasmon excitation of WO_{3-x} nanowires may be attributed to not only photothermal effect to the solution. As is well known, the plasmonic heating is highly localized on the surface. Therefore, upon plasmon excitation of WO_{3-x}, the local temperature nearby Pd nanoparticles on WO_{3-x} surfaces might be much higher than the tested solution temperature (60 °C), resulting in higher reaction efficiency.

Based on the above observations, we suggest that the plasmon excitation of WO_{3-x} nanowires enhances Suzuki coupling on Pd nanoparticles possibly through two ways, photothermal effect and assisting charge transfer. The principle is illustrated in Fig. 5. First, the photothermal effect by conversion of photons to thermal energy would increase the local temperature nearby Pd nanoparticles on WO_{3-x} nanowires, which results in enhancement of Suzuki coupling reaction on Pd. Second, the plasmon excitation of WO_{3-x} creates strong localized electric field and hot-electrons at Pd-WO_{3-x} interface, which would increase the charge density on Pd surface and assist the charge transfer between the Pd surface and reagents for Suzuki coupling to enhance the reaction. Similar explanations about plasmon-assisted charge transfer were also reported recently by others [19,20].

4. Conclusions

In summary, the plasmonic WO_{3-x} nanowires loaded with Pd nanoparticles retain strong LSPR absorption in the visible and NIR region. The LSPR excitation of the WO_{3-x} nanowires by long wavelength irradiation greatly promoted the Suzuki cross coupling reactions catalyzed by Pd nanoparticles in terms of the main product yield and selectivity, which could be attributed to the photothermal effect with strong localized plasmon heating on the WO_{3-x} nanowire surface. This paper is important because we demonstrate for the first time that the plasmonic effect of WO_{3-x} nanowires provides substantial enhancement on the reactions occurring not on WO_{3-x} surfaces, but more importantly, on the Pd nanoparticles attaching WO_{3-x} surfaces. Significantly, our studies reveal that the contributions of LSPR are not only limited to the reactions directly involving the plasmonic structure itself, but also capable of influencing the reactions catalyzed by the third-part materials (e.g., metal catalyst) attached on the plasmonic material surface. Therefore, this work opens a new LSPR-based strategy of using low-energy photons to facilitate catalytic reactions toward high yield and selectivity.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2015.11.037>.

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